Thin Film High K Dielectrics for Integrated Passive Devices

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Abstract

Over the last several years, there has been increasing interest in ferroelectric and related complex oxide thin films for a variety of applications. ATMI has developed a novel liquid delivery system for injection of low-volatility chemical precursors into metalorganic chemical vapor deposition (MOCVD) reactors in order to produce these multicomponent oxide thin films. They include $BaSrTiO_3$ (BST), $PbLaZrTiO_3$ (PLZT), and other related materials. $BaSrTiO_3$ (BST), which is used for integrated (DRAM) capacitors and memory elements, has reached the highest state of maturity. The authors have integrated the liquid delivery system with a commercial reactor capable of producing highly uniform films on 6" Si wafers at high rates. Charge storage densities up to 6,000 nF/cm² have been attained using extremely thin films of BST. Dielectric constants range from 20 to over 500, depending on composition and processing, with Q factors as high as 500 at kHz frequencies and X7R or better temperature specification. The performance of BST at frequencies up to the GHz range, and its suitability for integrated passive devices at high frequencies including switched capacitor filters and decoupling capacitors will be discussed in this work. There will also be discussion of potential commercial markets and manufacturing feasibility for these materials.

Key words:

High Frequency, Integrated Capacitor, Nonlinearity, Thin Film, $BaSrTiO_3$.

1. Introduction

With the increasing maturity of complex oxide thin film formation brought on by research into HTSC materials, there has been growing interest in other related multicomponent oxide materials for different applications. Major material systems include $BaSrTiO_3$, $PbLaZrTiO_3$, $SrBi_2Ta_2O_9$, conducting oxides ($LaSrCoO_x$), and magnetoresistive oxides ($LaCaMnO_3$,

$LaSrMnO_3$). These materials have a variety of uses including frequency doubling, optical switches, barrier layer, magnetic storage, microwave phase shifters, filters, and capacitors used for both volatile and nonvolatile memory elements. Many of these devices have particular relevance to the fast-growing portable electronics market which requires small sizes of components, increased functionality, and operation at high frequency. This paper will concentrate on capacitor applications of $BaSrTiO_3$ (BST) thin films and production of these thin films via metalorganic chemical vapor deposition (MOCVD).

Of these complex oxides, thin film technology for producing BST is the most advanced since numerous DRAM manufacturers are investigating this material for 1 and 4 Gb DRAMs (a potential market estimated to be in excess of $20 billion)[1]. While bulk barium titanate ceramic capacitors may seem like a mature technology, the range of properties available when producing this family of materials in thin film form is astonishing. Dielectric constant can vary by 2 orders of magnitude while resistivity (leakage current) can vary by up to 9 orders of magnitude. All depend on choices of composition and processing conditions when making the thin films. This range of properties is directly related to the variation in microcrystalline properties achievable in a thin film which can be formed in a metastable state (a condition difficult to achieve in bulk ceramics).

The semiconductor industry's movement to higher levels of integration has resulted in the gradual displacement of physical vapor deposition processes by chemical vapor deposition (CVD) for several reasons. This can be attributed to the ability to conformally coat small features with challenging aspect ratios (crucial for DRAMs). This has one of the highest throughput of any thin film deposition method, and a common use on different platforms in the semiconductor industry. For example, several groups have demonstrated that sputtered $BaSrTiO_3$ (BST) films do not have sufficient step coverage to be used alone in high density DRAMs[2,3]. Consequently, significant effort is being directed at the development of CVD processes for a variety of ferroelectric thin films;[4-6] however, progress has been slow. In general, the CVD processes exhibit poor thickness and composition precision arising from the use of solid and low vapor pressure liquid source reagents which are difficult to deliver by conventional methods.

Present CVD processes in widespread use in semiconductor manufacturing such as CVD W, Si, and SiO_2 utilize gaseous or high vapor pressure source reagents whose delivery can be easily controlled with standard mass flow controllers or bubblers. In contrast, high vapor pressure source materials are typically not available for many of the elements present in ferroelectric thin films. The problem of composition control for multicomponent films is further compounded by the number of elements to be deposited. In addition, many ferroelectric materials are not thermodynamically stable as a single phase over wide compositional ranges. The presence of non-stoichiometric material can cause dramatically different electrical properties in a thin film. For example, the authors have observed that a 3% change in Group II/Ti ratio away from perovskite in BST can cause a 2x decrease in dielectric constant and even larger changes in leakage. This is sensitivity to composition considerably greater than seen for bulk counterparts.

Over the last several years, ATMI has had a variety of programs underway which examined complex oxide thin films for a variety of applications. During this time, a metal organic chemical vapor deposition (MOCVD) process technology which utilizes liquid source reagent solutions consisting of solid source reagents dissolved in organic media to achieve excellent thickness and composition precision has been developed[6,7,10]. This technique overcomes the limitations of conventional delivery methods by controlling composition through real time volumetric mixing of the individual source reagent solutions. The liquid mixture is then flash vaporized to generate a homogeneous gas at the inlet to the CVD tool. This method minimizes the thermal budget of the thermally labile source reagents and ensures process reproducibility as well as simplifying reactor design by reducing sections requiring temperature control. Thus, it holds advantages for deposition of both simple oxide thin films, such as Ta_2O_5 and RuO_2, and more complex materials with higher dielectric constants and/or ferroelectric properties.

2. Experimental Work

All thin films discussed in this work have been deposited in a modified Watkins-Johnson (WJ) Select CVD reactor. It has been converted at ATMI through addition of a temperature controlled chamber, including a showerhead type gas distributor which gives uniform films over 6" substrates. The reactor is operated at low pressure, typically 750 mTorr, with 500 sccm each of oxygen and nitrous oxide as oxidizers. Substrates are either Pt/Ta/SiO_2/Si or Pt/SiO_2/Si. Top electrodes for capacitor electrical measurements are Pt deposited at 300°C by evaporation through a shadow mask.

Attached to this reactor is an ATMI LDS-300B liquid delivery system. This system injects MOCVD precursors dissolved in an organic solvent into an Argon (Ar) carrier gas stream which transports them into the reactor. Precursors for BST growth are Ba(thd)$_2$-tetraglyme, Sr(thd)$_2$-tetraglyme, and Ti(i-OPr)$_2$(thd)$_2$. Delivery rates of the precursor to the reactor average around 60 µmol/min. The details of the CVD reactor and the range of deposition conditions investigated have been described in a previous publication[1].

The BST thin film stoichiometry was $Ba_{0.45}Sr_{0.55}TiO_3$, as measured by x-ray fluorescence (XRF). Electrical measurements were made via an HP 4192A LCR meter and a HP 4145B parameter analyzer at ATMI. Dielectric nonlinearity measurements were made at Lucent.

3. Results

Dielectric constant in BST thin films can range from 15 to 1200, depending on growth conditions used. Losses as low as 0.3% (Q factor over 300) at frequencies above 1 GHz have been measured in films grown at ATMI. Tan δ is routinely below 0.002 at kHz frequencies[12]. Conductivity can range from semiconducting to leakage currents of under 10^{-9} A/cm² in layers as thin as 300 Å, depending on growth conditions and stoichiometry (with breakdown fields ranging from 0.2 to 2.5 MV/cm). The authors have recently attained capacitances per unit area as high as 100 fF/μm² (10 μF/cm²) in BST films. ΔC/C values as low as ± 15% over a temperature range from 25 to 300°C, combining essentially X7R performance with the prospect of extremely high capacitances per unit area in thin films have been demonstrated. Simple calculations using the properties reported show that BST thin film based capacitors offer compelling size advantages for operational voltages under 10 V and capacitance values below about 100 nF. Assuming a typical dielectric constant of 200, operational voltage of 5 V, breakdown voltage of 0.5 MV/cm, and a 250% safety factor, one can calculate the expected size of such a device. Figure 1 shows a comparison of BST thin films to the smallest commonly used commercial surface mount device (SMD) capacitors (0402 and 0604). The advantage of a thin film based capacitor is that it becomes smaller in size with smaller capacitance values, and conventional SMD devices do not. Since the 0402 device nears the limit of reliable automated pick-and-place on circuit boards, integrated thin film capacitors must be pursued in order to proceed beyond this scale. The size advantages achievable with thin film devices means that an entire network of small capacitors, such as the 50 pF size, often used in cellular phones can fit into the space of a single typical SMD.

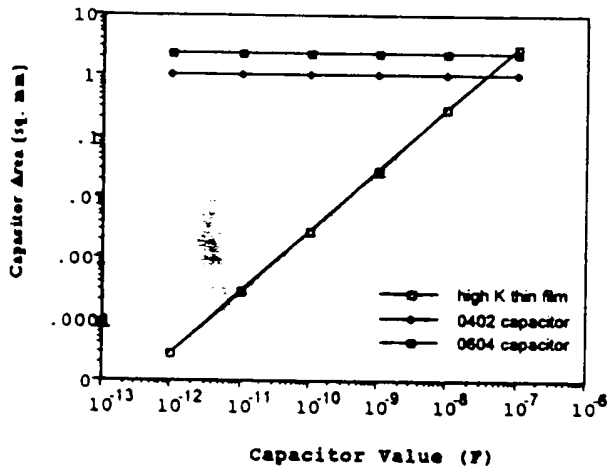

Figure 1. Plot of area required for various capacitor values, showing the compelling size advantage an on-chip thin film based capacitor can have over conventional discrete 0402 and 0604 size packages for small (<100 nF) capacitance values and low (5 V) voltages.

Having developed BST thin film deposition technology for DRAMs, the authors are now considering these films for a wider variety of applications in integrated passive devices. The work reported here was the outgrowth of a program with AT&T to develop on-chip thin film capacitors to replace discrete devices currently used for various power conditioning tasks. Each application has different requirements, as outlined in Table 1. Operation at 3 V is envisioned with the desire to withstand up to 9 V without device damage.

Most of the specifications in Table 1 are straightforward, but the voltage dependence of K requires some explanation. The second order dielectric nonlinearity, or a_2 value, is defined as shown in the polynomial equation, equation (1), where ΔC is change in capacitance with applied voltage V. The a_1 coefficient can be compensated for in most applications through design of matched capacitors, but a_2 cannot.

$$\Delta C/C = a_1 V + a_2 V^2 + \qquad (1)$$

Ideally, one would produce each of the three types of capacitor in Table 1 via the same MOCVD process and during the same thin film deposition run. Thus, a process/material combination must be found which meets all criteria simultaneously. An important variable in growth of BST films is the substrate temperature during growth. A high growth temperature promotes formation of crystalline material, resulting in a high dielectric constant. While at low temperatures, microcrystalline or amorphous material is formed which has much lower dielectric constant with lower leakage as well[13]. For this reason, the authors have chosen to focus on substrate temperature during growth for this study.

In addition to deposition temperature, bottom electrode and top electrode processing can have strong influences on measured film properties. An anneal after deposition of top electrodes can improve and stabilize measured electrical properties. In Figure 2, the authors compare films with no post-anneal, an oven anneal at 550°C for 1/2 hour, and a rapid thermal anneal (RTA) for 1 minute at 650°C.

Either type of anneal seems to significantly reduce leakage current in most cases, sometimes up to several orders of magnitude. The effect is particularly pronounced with the films deposited at higher temperatures where higher dielectric constants

Table 1. Typical performance parameters needed for a thin film based switched filter capacitor (SCF), bypass capacitor, and feedthrough capacitor used in an on-chip application.

	SCF	Bypass	Feedthrough
Capacitance density (fF/μm²)	>2.5	>2	>2
Frequency range	>100 MHz	2-3 GHz	2-3 GHz
Voltage dependence of K	a_2 < 100 ppm	N/A	a_2 <0.3%
DC leakage (A/cm²)	$<10^{-4}$	$<10^{-4}$	N/A
Q factor (inverse of loss)	100	50	50

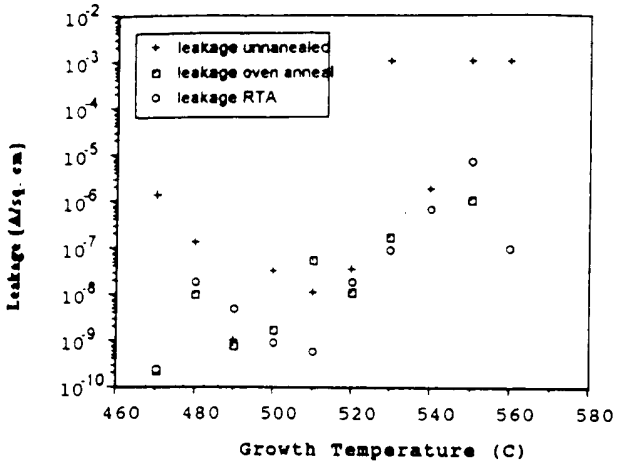

Figure 2. BST growth temperature vs. measured current leakage at 3 V in BST films ~480 Å thick. Comparison is made between different methods of thermal processing after deposition of top electrodes: none, oven anneal, and RTA.

and higher leakages are found. However, there is little or no difference between the two types of anneal. It was found that breakdown voltage correlates strongly with leakage; higher leakage tends to lead to lower breakdown voltages. Another effect noted was that leakier films have tendence to have "soft" breakdowns. As voltage was increased, current saturated at the compliance limit of the analyzer (10 mA) but the material regained its original properties upon reduction of voltage. On the other hand, lower leakage films could withstand more voltage, but they tended to fail more catastrophically.

Examination of the effect of the anneal on dielectric constant gave similar results; however, they were less pronounced. There was some improvement with any anneal, but little difference between the types of anneal performed.

When capacitance per unit area is calculated by combining breakdown voltages (based on associated leakage currents) with dielectric constant for these films, one finds no strong trend in storage density (F/cm^2) with deposition temperature. The reason is that low temperature BST growth gives higher breakdown voltages, so thinner dielectric films, as well as lower dielectric constants, compared to high temperature growth for little net effect. BST material properties, in principal can be adjusted based on the needs of a specific application, mainly for enhancement of other effects such as the low second order dielectric nonlinearity requirement mentioned in Table 1. Figure 4 shows this value as a function of film deposition temperature.

Second order nonlinearity can be reduced considerably by adjustment of the BST film properties via growth temperature reduction (Figure 4). The value of 0.2% for the lowest temperature films indicates that this material can be used for both bypass and feedthrough capacitor applications, though not SCF.

As shown, there is no strong dependence of charge storage for BST thin films with deposition temperature at these low processing temperatures and permittivity values. The advantage is that one can move to different regions of parameter space to optimize for different properties. Thus, if low change in dielectric constant with applied field is desired (such as for the feedthrough capacitor application which calls for a low a_2 parameter), a low growth temperature may be used. Conversely, for DRAMs, higher growth temperatures are used since operational voltages are very low and high dielectric constants are much more important than dielectric linearity.

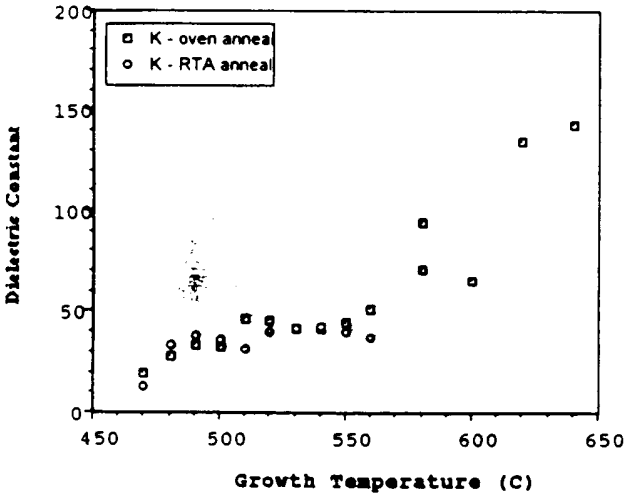

Figure 3. BST growth temperature vs. dielectric constant in BST films ~480 Å thick. This shows that variation of K by almost an order of magnitude is possible by varying growth temperature with more profound effects at the higher and lower temperature ends of the range investigated.

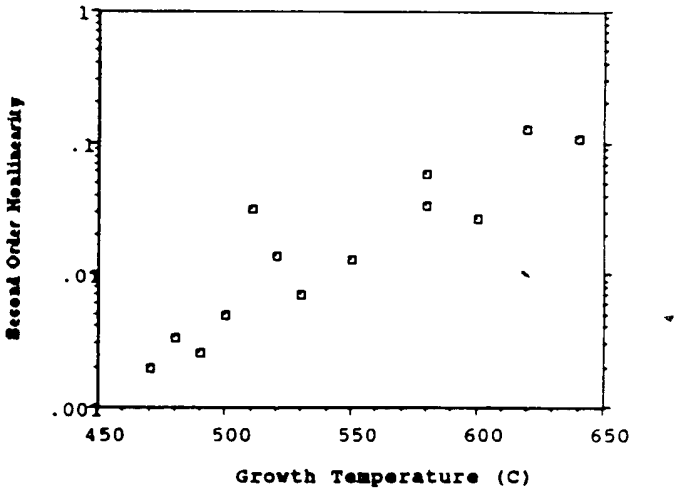

Figure 4. BST growth temperature vs. dielectric nonlinearity a_2 in BST films ~480 Å thick. This shows that reduction of a_2 by several orders of magnitude is possible by lowering growth temperature, satisfying specifications for feedthrough capacitors but not SCF devices.

4. Conclusions

An important requirement for use of these complex oxides in devices is the ability to provide a robust process for manufacture. Metalorganic chemical vapor deposition (MOCVD) is likely to be the method of choice for these processes. ATMI has demonstrated a precursor delivery system which utilizes liquid source reagent solutions to enable practical MOCVD of complex oxide materials[11].

The tremendous range of properties that may be attained for BST shows that this material can have many applications. Specifically, the authors have demonstrated the properties needed for use in bypass and decoupling capacitors. Switched capacitor filters will require further reduction of second order dielectric nonlinearities. This may be achieved by moving to higher Ti content BST materials.

In conclusion, the maturity of BST-based thin films shows that they are ready to replace lower dielectric constant materials in high density passive R/C networks and other integrated devices such as DRAMs. A number of other complex oxides are only a few years away from commercial use.

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13. It is likely that at deposition temperatures below 500°C significant C incorporation in the form of carbonates takes place.

About the Authors

Dr. Stauf received his B.S. in Chemical Engineering from Georgia Tech, following which he attended Syracuse University to attain an M.S. and a Ph.D degrees in Solid State Science and Technology. His dissertation related to decomposition studies and MOCVD of metal and metal silicide films using novel chemical precursors. Following this, he pursued a 2 year Research Associateship at the Naval Research Laboratory, studying MOCVD of low-bandgap InSb for infrared detectors using novel Sb precursors. After moving to

ATMI as a Research Scientist, he worked on MOCVD of BiSrCaCuO high-temperature superconductor films on wires, as well as on a variety of complex oxide layers on Si and other substrates for barrier layers, optical and electronic functions. Most recently he has been developing processes to deposit ferroelectric thin films (in particular BaTiO3 and BaSrTiO3) for use in DRAM and high frequency integrated capacitors, microwave phase shifters, and flat panel dielectrics. He is author of 32 technical papers and 3 patents, and is a member of IMAPS, MRS, and AVS Societies.

Dr. Steven Bilodeau is a research engineer at Advanced Technology Materials Inc. in Danbury, CT. After acquiring a Ph.D. in Materials Engineering from Rensselaer Polytechnic Institute in 1986, he was engaged in thin film research and development at Perkin Elmer, Hughes Danbury Optical Systems for several years. After joining ATMI, he has developed processes for a wide range of ferroelectric multicomponent oxides for electronic and optoelectronic applications. He is author of 21 technical papers and is a member of SPIE and MRS Societies.

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